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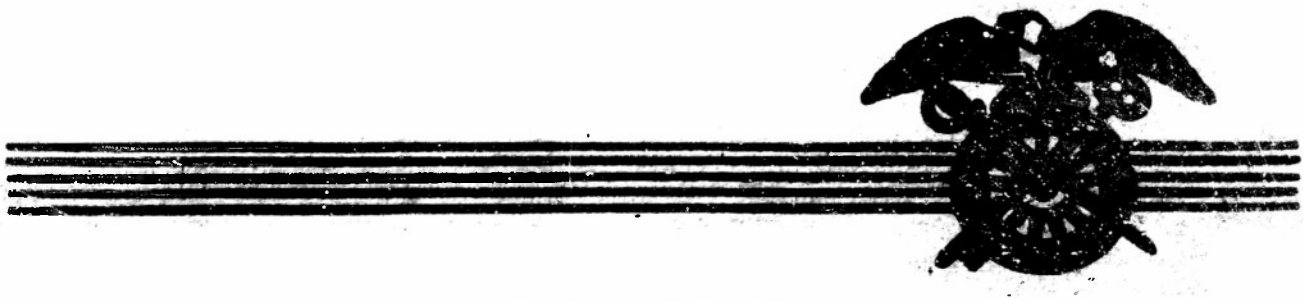
MECHANICAL PROPERTIES OF DECRYSTALLIZED COTTON

by

GEORGE SUSICH



DEPARTMENT OF THE ARMY

OFFICE OF THE QUARTERMASTER GENERAL

Office of The Quartermaster General
Research and Development Division
Textiles, Clothing and Footwear Branch

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Foreword

As part of its coordinated program of textile research, the Quartermaster Corps undertakes the evaluation of experimental fibers in order to determine their applicability for military fabrics. Work in the field of new fibers in recent years has been concerned mainly with synthetics, man-made and modified natural fibers. The Southern Regional Research Laboratory of the U. S. Department of Agriculture, in New Orleans, La., has developed a treatment for cotton fibers which increases their extensibility without lowering their tenacity. The modification is brought about by an amine treatment which reduces the originally high crystallinity of native cotton.

The investigation described in this report was undertaken to determine the mechanical properties of an amine treated(decrystallized) cotton yarn. The treated sample was furnished by the Scuthern Regional Research Laboratory.

Testing procedures developed in recent years in the Quartermaster Research and Development Laboratories have been applied in this study to investigate the change in the original properties of cotton brought about decrystallization.

The results reported herein have been discussed with Dr. K. Ward, Jr., of the Institute of Paper Chemistry, Appleton, Wisconsin, and with Dr. C. M. Conrad, and Mr. L. Segal of the Southern Regional Research Laboratory, New Orleans, La. Their valuable suggestions, which have been included in the final presentation, are gratefully acknowledged. The experimental work was performed with the assistance of Miss E. Th. Vadala and Mr. W. Zagieboylo, the graphs were drawn by Mr. J. Medernach and the report was reviewed by Mr. N. E. Roberts, all of the Quartermaster Research and Development Laboratories.

S. J. KENNEDY
Research Director
for
Textiles, Clothing and Footwear.

April 1953

ABSTRACT

The alteration of a cotton yarn by the amine treatment developed in the Southern Regional Research Laboratory was investigated.

The crystallinity of native cotton is markedly reduced after swelling in primary lower amines without affecting the structure, orientation or degree of polymerization of the cellulose I. Decrystallization increases the extensibility and the work necessary to rupture without lowering the tenacity. Enhanced extensibility is attained mainly by increased permanent set. Nevertheless the elastic recovery is higher after decrystallization if compared at identical strain levels. The elastic recovery of decrystallized cotton increases when wet. The excellent knot and wet behavior of native cotton fibers remain unaltered, but resistance to abrasion decreases after the amine treatment.

Decrystallized cotton has a combination of properties, some advantageous, others not, in comparison with native cotton and other textile fibers.

Introduction

Native cotton fibers contain a high percentage of crystalline cellulose I.* According to a recent compilation of Ward,[10] 88–94% "crystallinity"** of cotton has been found by chemical methods and 58–87% by physical methods. The remaining percentage of cellulose I is present in amorphous form readily accessible for chemical reactions, e. g., acid hydrolysis. The mechanical properties of cellulose fibers are markedly affected by the ratio of the crystalline to the amorphous portion. This is not unusual for organic high polymers showing visco-elastic behavior.

The crystallinity of cotton can be greatly reduced mechanically by grinding in a ball mill or in a vibratory mill, thus destroying the fiber structure. It can also be reduced by topochemical reactions.*** The mercerization of cotton is the best known of such processes, transforming cellulose I into cellulose II. Topochemical reactions of cotton are mostly connected with lateral swelling and shrinkage in the direction of the fiber length. This axial shrinkage (and disorientation of crystallites) can be compensated for (or over-compensated for) by stretching.

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* The nomenclature of P. H. Hermans[3] is used.

** The expression "crystallinity" is an approximation, and designates the ordered regions of cotton similar to the crystal lattice of perfect crystals. These regions correspond to the "inaccessible" part of cotton as revealed by chemical reactions. On the basis of our present knowledge, neither exact description nor correct measurement of the structural order present in cotton is possible. This explains the marked differences in "crystallinities" observed using various methods.

*** Topochemical processes (Kohlschuetter) are heterogeneous chemical reactions in which at least one component remains in the solid or swollen state.

If the cellulose I present in cotton fibers is dissolved (by xanthation, sulfuric acid, cuprammonium, etc.) and then regenerated in the form of fibers (viscose, Bemberg rayon), the fibers contain cellulose II with relatively low crystallinity: 67--79% when determined by chemical methods and 20-52% by physical methods.[10] Stretching does not affect the crystallinity of these fibers; it does produce, however, an alignment (orientation) in the crystalline and amorphous portions of the cellulose. The crystallinity of regenerated cellulose fibers can be increased by swelling agents[4,5] especially in connection with heat if marked chemical decomposition is thereby avoided. This process is known as recrystallization and is analogous to the recrystallization of metals by heat causing marked alterations of their mechanical properties.

Cotton is a fiber with relatively low extensibility. Its extensibility is sufficient, and even advantageous, for many end uses, but necessarily prohibits its application where high extensibility is required. Man-made fibers like rayon can be produced in different types to suit widely varied needs. They have either high extensibility and relatively low breaking tenacity, or rather low extensibility with high tenacity. Generally, high tenacity and high extensibility are desired, but it is difficult to obtain both within practicable limits. They increase the energy necessary for rupture and improve the performance in service if they are attained without markedly affecting other advantageous properties (e.g., the elastic recovery). Some special types of rayon developed in the past years represent compromises between these conflicting requirements, having the advantageous combination of high breaking tenacity and high (or, at least, not markedly diminished) extensibility.

Amine Treatment

Recently a treatment of cotton was developed in the Southern Regional Research Laboratory, New Orleans, La., with the object of increasing the elastic recovery of cotton without decreasing its breaking tenacity. This process increases the extensibility of native cotton fibers and reduces their rather high crystallinity using lower aliphatic amines as swelling agents. This amine treatment of Segal, Nelson, and Conrad[6] is the subject of the US Patent 2,580,491 "Reducing the Crystallinity of Native Fibrous Cellulosic Materials,"[11] and is based partly on the investigation of Davis, Barry, Peterson, and King.[2]

The amine treatment is carried out by swelling cotton (staple fibers, spun yarns) in liquid anhydrous ethylamine, preferably at ice bath temperature, removing the swelling agent by extraction with chloroform or hexane, and drying. Reduction in crystallinity in varying and controllable degrees can also be obtained by propylamine, and — after preswelling with methyl or ethylamine — by other anhydrous lower primary alkylamines (up to heptylamine) or by their mixtures, e.g., 75% ethylamine and 25% hexylamine.

The X-ray diffraction studies of Davis, Barry, Peterson, and King[2] revealed that the swelling of cotton in amines is connected with considerable structural changes due to a reversible topochemical reaction which can be best understood by formation of hydrogen bonds between the hydroxyl groups of cellulose and the amino group of the amine -O-H——N-. The cellulose amine compound is relatively unstable and it is decomposed (again by a topochemical reaction) upon removal of the amine by non-polar liquids re-forming cellulose I without destroying the fiber structure.

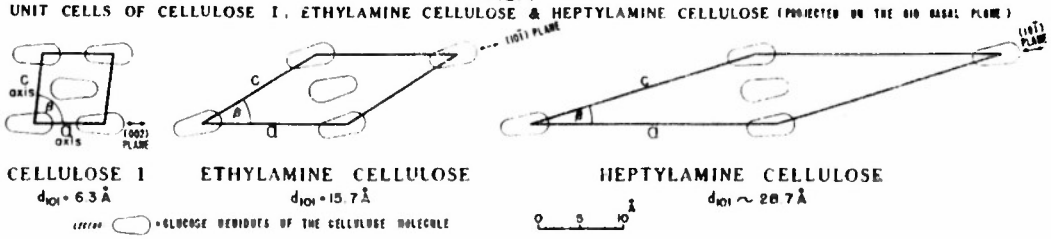
The crystal lattice of amine-swollen cellulose is analogous to that of ammonia cellulose thoroughly investigated by various authors (Hess and Gunderman; Clark and Parker; Barry, Peterson, and King [1]).

Figure 1 demonstrates the basal (010) planes of the unit cells for cellulose I, ethylamine cellulose and heptylamine cellulose. In the two latter patterns only the glucose residues of the cellulose molecules are shown and the amines are omitted. It is apparent that the addition of the amines causes a great distention of the lattice. The a and c axes and the volume of the unit cells (the area of the basal planes) increase considerably. The β angle (between the a and c axes) markedly diminishes and the glucose residues of cellulose are turned from their original positions (in 002 planes) into $10\bar{1}$ planes, forming hydrogen bonds with the amines.

In Figure 2 the crystal lattices of cellulose I and ethylamine cellulose are depicted, again with omission of the amine molecules which lie between neighboring glucose residues in the empty spaces of the $10\bar{1}$ lattice planes. The 010 basal planes demonstrated in Figure 2 are perpendicular to the chain length of cellulose molecules and to the fiber axis. The glucose residues are therefore shown as seen from the direction of the fiber length in cotton. They appear perfectly ordered in both cases demonstrated, but in different patterns. The crystal lattice is changed and greatly widened in the ethylamine swollen state.

FIG. 1

UNIT CELLS OF CELLULOSE I, ETHYLAMINE CELLULOSE & HEPTYLAMINE CELLULOSE (PROJECTED ON THE 010 BASAL PLANE)



CELLULOSE I $d_{101} = 6.3$ Å

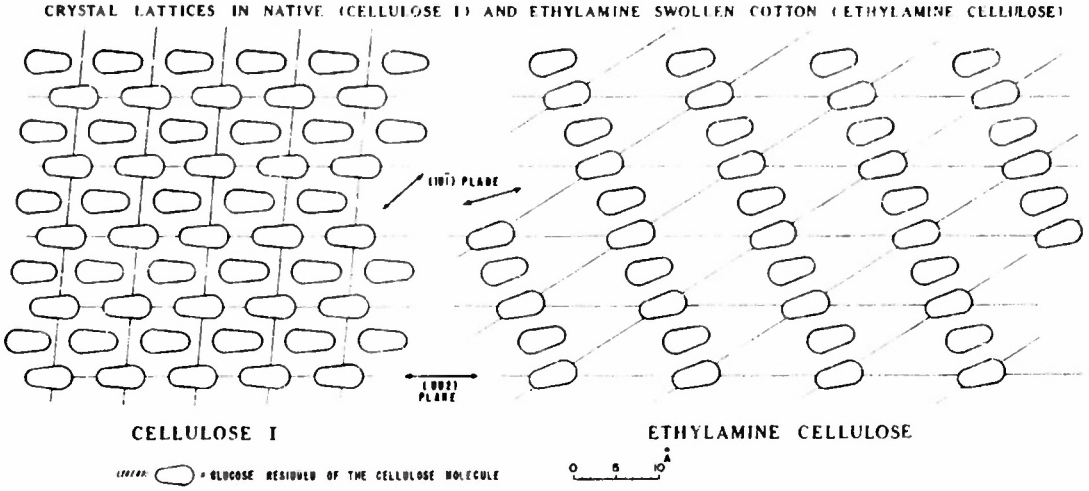
ETHYLAMINE CELLULOSE $d_{101} = 15.7$ Å

HEPTYLAMINE CELLULOSE $d_{101} \sim 28.7$ Å

= GLUCOSE RESIDUES OF THE CELLULOSE MOLECULE

FIG. 2

CRYSTAL LATTICES IN NATIVE (CELLULOSE I) AND ETHYLAMINE SWOLLEN COTTON (ETHYLAMINE CELLULOSE)



CELLULOSE I

ETHYLAMINE CELLULOSE

= GLUCOSE RESIDUES OF THE CELLULOSE MOLECULE

These structural differences are manifested by increased interplanar distances (d) of the equatorial 101 interferences without significantly affecting the position of the $10\bar{1}$ and

002 lines on the X-ray diagrams of amine swollen products. The distention of the cellulose lattice by amines thus occurs mainly between successive 101 planes and it increases with the length of the amine molecule. Each carbon atom of the straight alkylamine chain results in an increase of slightly more than 2 Å in the 101 interplanar distance (d_{101}). This indicates that two amine molecules are added to each glucose residue $C_6H_{10}O_5$. The fiber axis (b axis = 10, 3 Å, not shown in Figures 1 and 2) remains unaffected by the reaction with amines. This is not surprising because very strong bonds are present in this direction holding together the glucose residues in long-chain molecules of cellulose.

The amorphous (accessible) part of cotton may react first in the topochemical processes during swelling of cotton in amines and removal of the swelling agent. The crystalline part of cotton reacts too, however, as evidenced by the X-ray diffraction pattern of amine-swollen products. Reactions which distort the crystal lattice so greatly could hardly occur without affecting the high structural order (crystallinity) originally present in cotton. The amine treatment of cotton is, therefore, invariably connected with deterioration of the crystallinity.

It can be understood from the structural changes discussed that (1) no swelling of cotton occurs in aliphatic amines higher than heptylamine (by steric hinderance), and that (2) only lower amines are capable of swelling cotton directly. Amines higher than propylamine and bulky amines (e.g., isopropylamine) swell cellulose only after the lattice has been widened by a pre-treatment with ammonia or lower amines. This then permits the penetration of the cellulose lattice by larger amine molecules.

Known Properties of Decrystallized Cotton

According to Segal, Nelson and Conrad[6] the amine treatment of cotton decreases the original crystallinity (89-91%, measured by acid hydrolysis) to 20-40% without markedly altering the orientation and the degree of polymerization (e.g., 4680 before, 4550 after). Decrease of crystallinity can also be detected by loss in intensity and broadening of the equatorial X-ray diffraction lines 101, $10\bar{1}$, and 002 of cellulose I. It is noteworthy that amine-treated cotton retains the crystal lattice of cellulose I which is considered to be the less stable form of cellulose under normal conditions. In contrast, the treatment of cotton with alkalihydroxides (mercerization) or with

other swelling agents is invariably connected with the transformation of cellulose I into cellulose II. Decrystallized cotton is fairly stable after removal of the swelling agent and drying. Only partial recrystallization occurs even when boiled for hours in water. The cross section of amine-treated cotton is enlarged due to opening of the lumen. As can be expected, moisture regain increases (from 9 to 11-13% at 81% R.H.). Segal et al. [6] reported a marked increase in extensibility (from 5.8 to 13.3-17.1%) without appreciable loss in breaking tenacity (1.7 g/gx originally, 1.5-1.6 g/gx after decrystallization for a 20/1 yarn)*. This behavior is the most striking effect of the amine treatment, resulting in a considerably increased energy necessary for rupture.

Similar to amine-treated cotton, regenerated cellulose fibers (viscose, Bemberg rayon) and mercerized cotton have lower crystallinity and higher moisture absorption than native cellulose fibers (cotton, ramie, linen, hemp). It is appropriate, therefore, to compare the properties of decrystallized cotton with those of fibers containing cellulose II. The tenacity, extensibility and recovery of these fibers may vary widely depending upon the tension applied during fiber formation or during mercerization. The breaking tenacity and elastic recovery of stretched regenerated cellulose fibers markedly surpass that of cotton. However, their tenacity and extensibility when knotted is then diminished, which is not to the advantage of their serviceability. It is also characteristic for regenerated cellulose fibers that their tenacity decreases and their extensibility increases markedly when swollen in water. This does not contribute to the stability of their functional performance, either. The inherent abrasion damage of regenerated cellulose fibers is rather high compared to that of cotton. [8]

The crystallinity of cotton cannot be reduced or its extensibility enhanced without influencing other fiber properties. The purpose of the present study was to investigate the changes in some mechanical properties of cotton brought about by amine treatment.

Testing Procedure

The tensile characteristics (yield point, breaking tenacity, extensibility, initial modulus, work necessary for rupture,

* Increase of tenacity from 3.01 to 3.12 g/gx was observed for cotton single fibers. (Dr. C. M. Conrad)

tensile recovery including elongation components), knot behavior, wet behavior and flex abrasion damage of untreated and decrystallized cotton were investigated. These mechanical properties were thought to be critical factors in juding the potentialities of decrystallized cotton.

Test Conditions: Tests were performed under standard atmospheric conditions: 70 F (21.2 C) and 65% R.H.

All the tensile tests were made on the Instron tensile tester, with a 10.0-in. (25.4-cm) gage length, a jaw speed of 5 in. (12.7cm) per minute, (i.e., 50% elongation per minute), and a pretension of 5 g, which eliminates the crimp, 1.8% from the untreated yarn and 5.0 per cent from the decrystallized yarn. Ten individual samples were tested.

For the knot tests an overhand knot was tied by hand in a specimen of approximately 13 in. (33 cm) and tightened mechanically by three loading and recovery cycles between 0 and 50 g load. After a one-hour relaxation period without tension, tensile tests were made as above on the knotted samples.

The recovery was determined using a cycling procedure[7] which permits the separation of three elongation components - immediate elastic recovery, delayed recovery and permanent set. Between 9 and 17 individual specimens reflecting average behavior were extended to progressively increased strain levels. After extending the samples, a five-minute relaxation time was allowed without tension for delayed recovery.

Tests on wet fibers were performed (after the samples were swollen in water for one hour) using a water container attached to the Instron tensile tester.

The abrasion tests were made on the Stoll-Quartermaster abrasion tester. Yarn bundles, comprising different numbers of parallel yarn strands, were flex abraded using the same steel bar. The tests were performed at two different severities by changing the yarn pressure and tension: 0.5 lb (227g) and 2 lb (907 g). A stroke length of 0.5 in. (1.3 cm) (measured on the bar) and a speed of 120 double strokes (cycles) per minute were used. Five bundles with identical numbers of yarn strands were tested in each case. Further details of this experimental procedure will be given in a forthcoming Textile Series Report.[8]

Test Samples: Tests were performed on cotton yarns, untreated and decrystallized,* to permit easy comparison of the alteredpproperties. A 20/1 combed cotton yarn (nominal fineness 296 grex) without any finish, spun from 1949 Mississippi and Arkansas cotton full 1-1/32 in. (2.62 cm), strict middling color, with 13.4 turns per in. (5.28 turns per cm) twist (Wiscassett Mills Company, Albermarle, N.C.) served for this investigation. The decrystallized yarn was furnished by Dr. C. M. Conrad of the Southern Regional Research Laboratory and was prepared at an early stage of the study of the amine treatment.

Test Results

Tensile properties of the untreated and decrystallized cotton yarn in the original state, when knotted, and when wet, are shown in Figure 3 and Table I. The amine treatment caused shrinkage (approximately 10%) and crimp in the yarn. The shrinkage partly explains the higher actual grex of the decrystallized yarn. The amine treatment altered the morphology of the yarn (Figure 4), crimping it, loosening its structure, and roughening its surface.

Decrystallization does not significantly affect the yield tenacity (0.26 before and 0.22 g/gx after amine treatment); it increases, however, the yield elongation (from 2.8 to 6.6%), indicating an enhanced elasticity if compared at relatively low strain levels. Decrystallization greatly reduces the initial modulus of elasticity (from 70 to 17 g/gx), which is probably disadvantageous for some end uses. The considerably higher extensibility after decrystallization (17.3 compared to 9.1%) at practically unchanged breaking tenacity (1.53 and 1.43 g/gx) markedly increases the work necessary for rupture (from 5.4 to 9.1 gcm/gx for 1 m fiber length).

It is characteristic of cotton that if knotted, the breaking tenacity and extensibility do not decrease significantly. This manifests its resistance to high stress concentrations and to bending and shearing forces. The essentially unchanged relative

* The results obtained reflect only partly the inherent properties of cotton fibers, since they are influenced by the form factors (yarn size, twist, etc.) of the yarns. These were, however, almost identical for the two yarns tested and their influence does not prohibit valid comparison of altered properties due to reduced crystallinity.

FIG. 3

STRESS - STRAIN CURVES

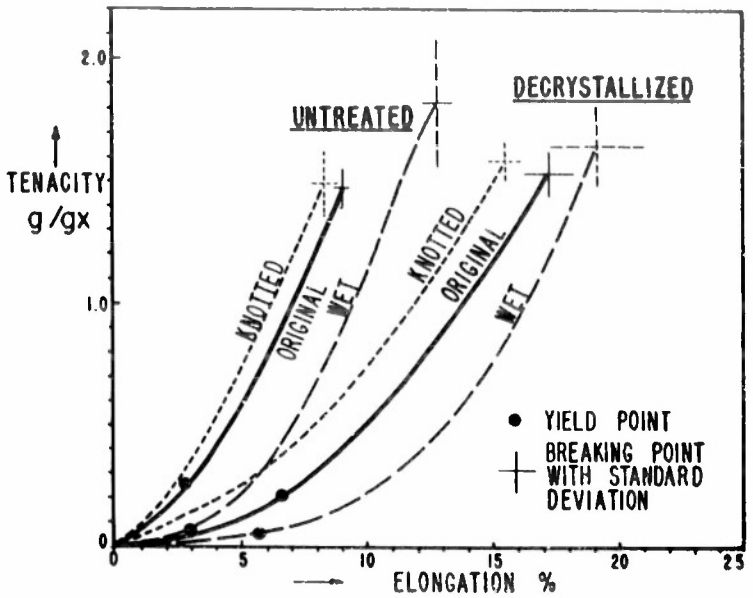


FIG. 4

MACROGRAPHS OF YARNS

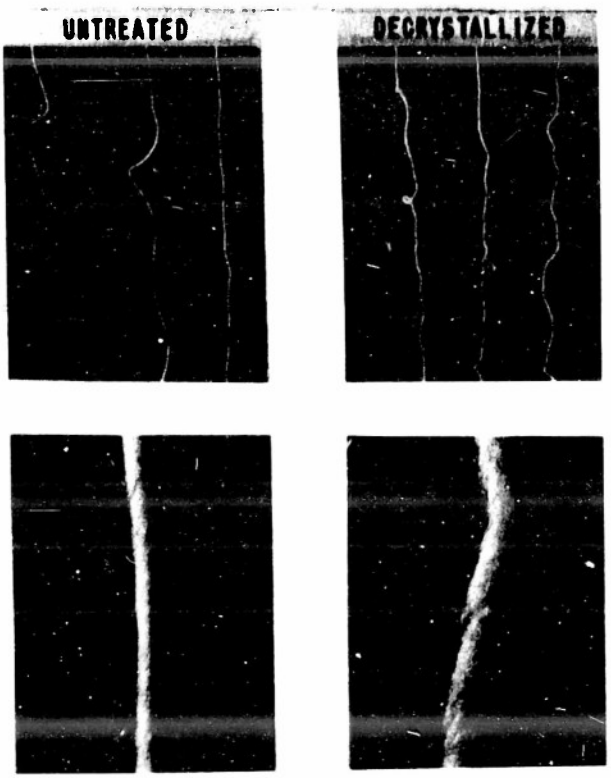


TABLE I

Tensile Properties

	Untreated Cotton Yarn (297 gx actual fineness)			Decrystallized Cotton Yarn (350 gx actual fineness)		
ORIGINAL						
Yield load[1]	78	g		77	g	
Yield tenacity[1)2)3]	0.26	g/gx		0.22	g/gx	
Yield elongation[1]	2.8	%		6.6	%	
Initial modulus of elasticity[3)4]	70	g/gx		17	g/gx	
Load at break	434	g		536	g	
Tenacity at break[2]	1.47	g/gx	(5.8)[8]	1.53	g/gx	(5.9)[8]
Elongation at break	9.1	%	(3.1)[8]	17.3	%	(5.6)[8]
Work of rupture for 1 m fiber length[7]	5.4	gcm/gx		9.1	gcm/gx	
KNOTTED						
Load at break	442	g		553	g	
Tenacity at break[2)3]	1.49	g/gx	(9.0)[8]	1.58	g/gx	(4.9)[8]
Elongation at break	8.4	%	(6.2)[8]	15.6	%	(4.8)[8]
Relative knot tenacity	102	%		103	%	
Relative knot elongation	92	%		90	%	
WET						
Yield load[1]	18	g		14	g	
Yield tenacity[1)2)3)5]	0.06	g/gx		0.04	g/gx	
Yield elongation[1)6]	2.8	%		5.8	%	
Initial modulus of elasticity[3)4]	22	g/gx		7	g/gx	
Load at break	540	g		575	g	
Tenacity at break[2)5]	1.82	g/gx	(14.4)[8]	1.64	g/gx	(10.0)[8]
Elongation at break[6]	12.9	%	(5.3)[8]	19.2	%	(9.8)[8]
Work of rupture for 1 m fiber length[5)6)7]	7.9	gcm/gx		7.9	gcm/gx	
Relative wet tenacity	124	%		108	%	
Relative wet elongation	142	%		111	%	

NOTES TO TABLE I

1) The yield point is identical here with the elastic limit and designates the stress and strain where permanent elongation starts. It was obtained from the analysis of the stress-strain curves (Figures 5, 6, and 7).

2) Uncorrected tenacities based on the initial fiber fineness are listed. They can be converted into corrected tenacities (based on diminished grex) by multiplication with $\frac{100 + E}{100}$, where E is the elongation expressed in percent.

3) Tenacity and initial modulus values expressed in grams per grex can be converted by multiplication with 1.11 into grams per denier (tenacity and modulus); with 10d into kg/mm^2 (tensile strength and modulus); and with 9.8d into 10^8 $dynes/cm^2$ (modulus). d = 1.52 density of cotton.

4) Initial modulus of elasticity was obtained graphically from the linear portion at the beginning of the stress-strain curves. Mostly higher values are obtained from the yield point.

5) Tenacity values of wet fibers are correlated to the dry fiber fineness.

6) Elongation of wet fibers are correlated to the wet length which was practically identical to the dry length.

7) Work expressed in gram centimeters can be converted by multiplication with 981 into ergs and with 2.34×10^{-5} into calories.

8) Figures in parantheses designate the coefficients of variations in percent for ultimate values obtained on ten specimens.

FIG. 5

RECOVERY BEHAVIOR DEMONSTRATED BY FOUR CURVES

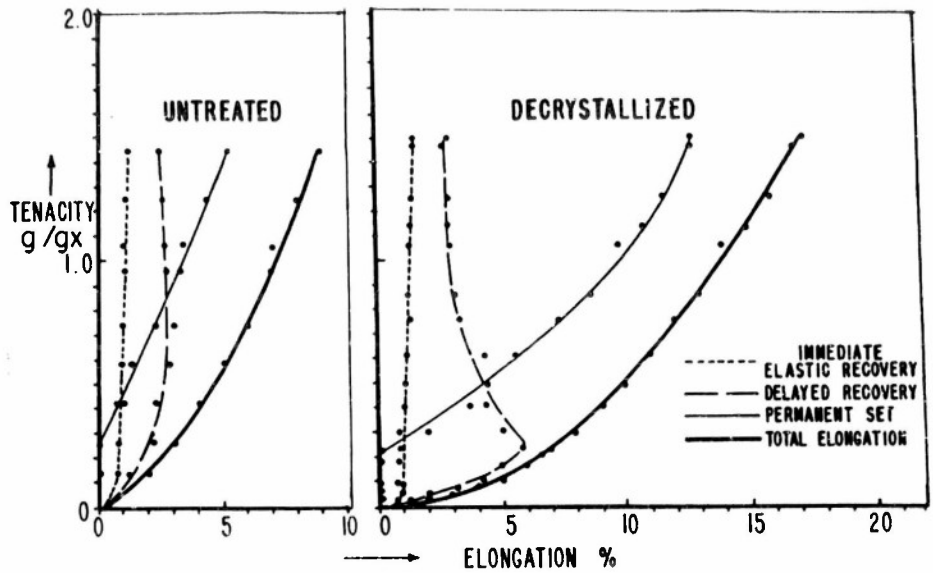
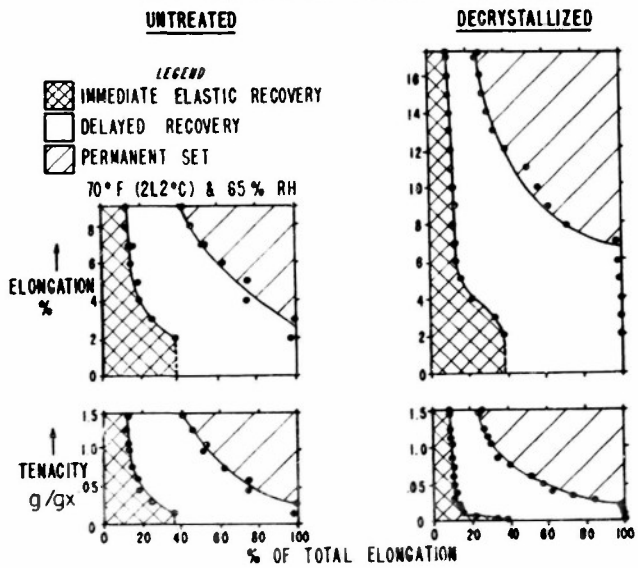


FIG. 6

RECOVERY BEHAVIOR DEMONSTRATED BY RECTANGULAR GRAPHS



knot tenacity (103 compared to 102%) and knot extensibility (90 compared to 92%) after decrystallization indicates that the excellent knot behavior of native cotton remains unaltered by decrystallization. This can be understood since the fibrillar structure (responsible for the good knot behavior of cotton) is not affected in the topochemical processes leading to decrystallization.*

It is a unique property of cotton that its tenacity and extensibility slightly increase when wet (i.e., to 124 and 142% of the dry values). No other textile material subject to swelling in water possesses this advantageous behavior. This characteristic remains at least partly unaltered since a relative wet tenacity of 108% and a relative wet extensibility of 111% were observed after decrystallization. Swelling considerably decreases, however, the initial modulus of untreated yarn (from 70 to 22 g/gx) as well as of the decrystallized yarn (from 17 to 7 g/gx). It also affects the work necessary for rupture enhancing that of untreated yarn (from 5.4 to 7.9 gcm/gx) and diminishing that of the decrystallized yarn (from 9.1 to 7.9 gcm/gx).

It is not enough to know what stress can be applied to a fiber and how much the fiber can be elongated without rupture. To estimate performance in service, some knowledge of recovery behavior is also necessary; it must be known to what extent and at what rate an imposed strain recovers after the stress is released. Great differences exist in the recovery of textile fibers and most of them recover almost entirely below the yield point. The immediately recoverable portion is, however, only a fraction of their total recovery. The permanent set (unrecoverable portion of the strain) generally starts at the yield point. It increases with increasing strain and stress up to the breaking point. Cotton is known to be elastic only at very low stress and strain levels, and its permanent deformation is comparatively high especially close to the breaking point limiting its dimensional stability. The elastic recovery of regenerated cellulose fibers varies widely and is usually not very good except for fibers with high tenacity and a rather low extensibility (high-tenacity viscose, Fortisan).

In discussing the tensile recovery behavior of untreated and amine-treated cotton critically, actual and relative values of the elongation components — immediate elastic recovery, delayed recovery and permanent set — must be considered at comparable levels from the onset of stretching up to rupture .[7] Results of recovery

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* The extensibility of the yarns appears reduced in knot tests, probably as a result of hindered slippage of individual staple fibers and/or of a slight "mechanical conditioning" in tying the knots.

tests performed on untreated and decrystallized cotton under standard atmospheric conditions using the Instron tensile tester are represented by four curves (Figure 5), rectangular graphs (Figure 6), and by numerical data (Table II).

TABLE II

Recovery Behavior at the Breaking Point

	Untreated Cotton Yarn		Decrystallized Cotton Yarn	
	Dry	Wet	Dry	Wet
Actual Values of Elongation Components in Per Cent of the Original Length*				
Immediate Elastic Recovery	1.2	1.7	1.5	2.3
Delayed Recovery	2.5	4.8	2.8	6.4
Permanent Set	5.4	6.4	13.0	10.5
Total Elongation	9.1	12.9	17.3	19.2
Relative Values of Elongation Components in Per Cent of the Total Elongation**				
Immediate Elastic Recovery	12	13	9	12
Delayed Recovery	28	37	16	33
Permanent Set	60	50	75	55

* Actual values are demonstrated in Figure 5.
** Relative values are demonstrated in Figures 6 and 7.

The elongation components observed show that the immediate elastic recovery remains practically unaffected by the amine treatment. The actual values of delayed recovery (Figure 5) appear higher after decrystallization up to approximately 0.7 g/gx tenacity and at any comparable elongation (up to the breaking elongation of the untreated yarn). The enhanced extensibility of the treated sample is thus due to increased delayed recovery up to these levels, corresponding to a remarkable part (46 and 53%)

of its breaking point. The unrecoverable elongation of decrystallized cotton starts at about the same stress but at notably higher strain than that of the untreated cotton (Figures 5 and 6). It increases at a high rate in the decrystallized yarn with increasing stress and strain up to the breaking point. The actual and relative values of permanent set are lower after decrystallization than originally when compared at identical elongation levels up to the breaking point of the untreated yarn (9.1%). Although the permanent set of the treated yarn is considerable at higher elongations (between 9.1 and 17.3%) no comparison with the untreated yarn is possible because these strains exceed its breaking point. The decrystallized yarn has, however, higher actual and relative values of permanent set than originally when comparison is made at identical stress levels. Actual and relative values of permanent set at the breaking point (shown in Table II and Figures 5 and 6) clearly demonstrate that the much higher extensibility of decrystallized cotton is obtained mainly by increased permanent deformations (from 5.4 to 13.0% for actual and from 60 to 75% for relative values).

The influence of decrystallization upon the recovery behavior in the wet state is interesting and is shown by numerical data (Table II) and by eight quadratic graphs in Figure 7. To facilitate a comparison, the relative values of elongation components are here plotted against percentage of elongation at break and tenacity at break. The areas representing the three elongation components appear only slightly altered for untreated cotton after swelling. Notable changes appear, however, for decrystallized cotton in the wet state. The higher extensibility of untreated cotton when wet is attained by increasing the actual values of all three elongation components approximately at the same rate. On the other hand, the recovery behavior of the wet decrystallized cotton is characterized by enhanced actual and relative values of delayed recovery and diminished permanent set. Decrystallized cotton thus becomes more elastic when wet similar to viscose rayon, but with the following difference: (1) the extensibility of wet viscose increases more than that of decrystallized cotton, and (2) it is accompanied by marked loss in tenacity. The recovery of decrystallized cotton after swelling is also analogous to that of protein fibers in that they are more elastic when swollen.[9] It is known that swelling in water enhances the elasticity of natural keratin fibers (wool, mohair, human hair) to such an extent that they become entirely elastic almost up to their rupture.

The beginning of permanent set on the eight quadratic graphs of Figure 7 indicates the elastic limit and the yield point. It also visualizes the previously discussed alteration of the initial

FIG. 7

RECOVERY BEHAVIOR (DRY & WET) DEMONSTRATED BY QUADRATIC GRAPHS

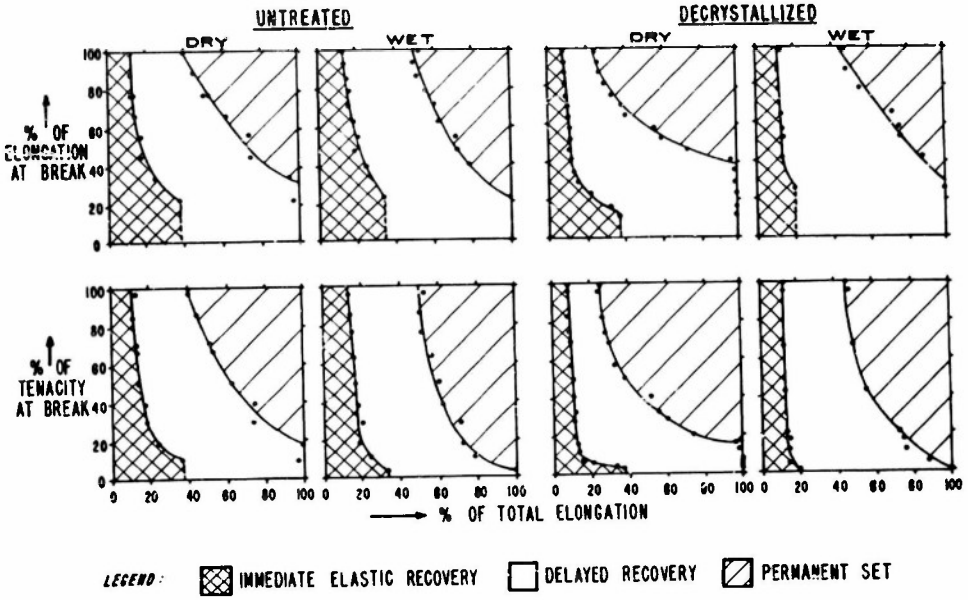
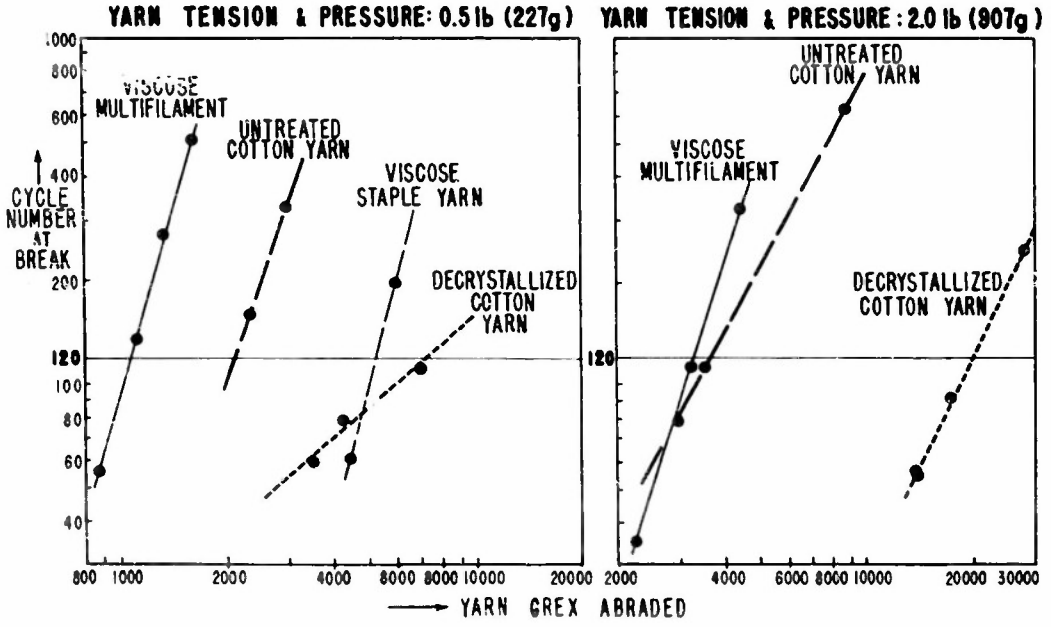


FIG. 8

FLEX ABRASIVE BEHAVIOR



modulus by swelling. This decreases considerably and approximately at the same rate for untreated and treated cotton in the wet state. It is the result of markedly diminished yield tenacity.

The abrasion behavior of textile fibers is a property affecting their wearing quality. Abrasion of untreated and decrystallized cotton was carried out on yarns to avoid the complicating factors of fabric texture, geometry and surface. The fiber damage in flex abrasion was measured quantitatively. Not cycle numbers at break, but rather weight per unit length (fiber grex) abraded after a constant number of cycles served as the basis for comparison.[8] The flex abrasion of a viscose staple yarn and viscose multifilament was included in this investigation for the sake of comparison.

The yarn grex abraded by 120 cycles in one minute was compared for each material. It was obtained by extrapolation from the observed cycle numbers at break as demonstrated in Figure 8 where a linear relationship appears between the logarithms of the cycle numbers and logarithms of the yarn grex. Table III shows that 2150, 7200, 5300 and 1100 grex were abraded in 120 cycles of the untreated cotton, the decrystallized cotton, the viscose staple, and the viscose multifilamentous yarns respectively, when tested at the milder severity (0.5 lb = 227 g yarn tension and pressure). The abrasive damage of decrystallized cotton was, therefore, 3.35 times higher here than that of the untreated yarns. At the higher severity (2.0 lb = 907 g yarn tension and pressure), a ratio of 1:5.40 was obtained.

The high abrasion damage of cotton after decrystallization, is, of course, disadvantageous. It is probably not only the result of increased permanent set due to diminished crystallinity (at least in the sample tested) but also of the altered yarn morphology after the amine treatment. The numerous single fibers not adequately attached to the yarn body (shown in Figure 2) can be easily pulled out or cut through in the flexing procedure. This causes an untwisting and a loosening of the yarn structure which increases the attrition additionally if tensional, compressional, bending and shearing forces act upon the yarn.

The abrasion damage of the yarns tested is compared in Table III to that of viscose staple yarn, which is known to be high.[8] Viscose multifilaments and untreated cotton yarn were found to suffer markedly less abrasion damage (0.20 and 0.40 respectively), while the decrystallized cotton yarns suffered slightly more (1.36) than viscose staple yarn.

TABLE III

Abrasion Damage

Material	Grex abraded in 120 cycles*		Relative abrasion damage compared to viscose staple yarn
Yarn Pressure and Tension:	0.5 lb (227 g)	2.0 lb (907 g)	0.5 lb (227 g)
Untreated cotton yarn	2150	3700	0.40
Decrystallized cotton yarn	7200	20000	1.36
Viscose staple yarn	5300		1.00
Viscose multifilament yarn	1100	3300	0.20

* Testing conditions are described in the text.

Summary

Reduced crystallinity increases the extensibility and the energy necessary for rupture and also improves the wet recovery of native cotton without markedly sacrificing its other advantageous properties. The good knot and wet behavior of decrystallized cotton is a result of unaltered fibrillar structure, unchanged cellulose I lattice and high degree of polymerization. The low initial modulus and the high permanent set of decrystallized cotton is disadvantageous if compared with untreated cotton at identical stresses and at the breaking points. The abrasive damage after amine treatment is also higher and similar to that of spun viscose. To what extent this latter deterioration is due to reduced crystallinity or to other factors which may be avoided in the amine treatment process is still a question.

Decrystallized cotton has thus a combination of properties not present in other textile materials. Some of them are desirable, others not. Its properties can probably be additionally altered either by controlled stretching during swelling, deswelling and drying or by other means (e. g., cross-linking). These might produce wide variations in the characteristics of the final products, making them suitable for some uses where cotton thus far has not been applied satisfactorily.

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